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The atmospheric carbon sequestration potential of man-made tidal lagoons

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Abstract

Understanding sequestration of carbon by coastal ecosystems is central to addressing the role they play in climate change mitigation. To quantify this process, accurate measurements of CO₂ fluctuation, coupled with variations in residence time of coastal water-bodies are required. Nearshore ecosystems, including coastal lagoons, may provide an effective sink for atmospheric carbon dioxide, particularly those containing productive biota such as seagrass. However, the rate and pattern of carbon sequestration in seagrass meadows across a range of environmental settings is still poorly constrained. In this study, we utilize a robust physical tidal model, along with biogeochemical dissolved inorganic carbon (DIC) assessment, to estimate water residence time and net sequestration of atmospheric CO₂ in an intertidal lagoon containing a seagrass (*Zostera noltii*) meadow. Total alkalinity and pH measurements taken from advected water mass exchanged with the open ocean at inlet boundaries are used to calculate DIC and pCO₂. A predictive model of hydrodynamics provides good approximation of mean water residence time to within 6 hr (± 3 s.d). Results indicate that during the daytime study period the lagoon is a sink for carbon, having a mean net ecosystem productivity (NEP) of 3.0 ± 0.4 mmol C m⁻² hr⁻¹. An equivalent diel NEP range of between 15.23 and -9.24 mmol C m⁻² d⁻¹ is calculated based on reported shallow water pelagic respiration rates. Moreover, approximately 4% of DIC availability occurs from atmospheric CO₂ transfer to lagoon water. However, a negative diel rate of -82 ± 81 mmol C m⁻² d⁻¹ is found, assuming overnight respiration ascertained from converted *Zostera noltii* O₂ utilization. We hypothesize that analogous regional

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nearshore ecosystems provide baseline study sites suitable to elucidate the carbon capture potential of planned, nearby tidal range energy schemes.

Keywords

Coastal lagoons; Atmosphere-ocean carbon exchange; Tidal energy; Carbon sinks; Dissolved Inorganic Carbon; Irish Sea coastal modelling

1. Introduction

Coastal lagoons, saline ponds and barrier systems occupy around 13% of coastal areas worldwide and accommodate important productive habitats such as seagrass meadows (Barnes, 1989). Despite their sparse ocean coverage (<0.2%), seagrass meadows play an important role in carbon sequestration and burial, estimated to be between 20 and 112 Tg C yr⁻¹ (Duarte et al., 2010; Kennedy et al., 2010; Fourqurean et al., 2012). However, not all seagrass meadows are net autotrophic (Duarte et al., 2010); many nearshore coastal ecosystems are thought to contribute to atmospheric CO₂ levels by acting as a net source, with heterotrophic processes that produce CO₂ outweighing autotrophic processes that consume it (Mork et al., 2016). Coastal lagoons can be productive environments due to high nutrient levels in both sediments and water, and are frequently colonized by benthic plants due to suitable sunlight penetration in the shallow water column. They represent a valuable resource for both fisheries and blue carbon initiatives, supported by research finding that shallow water autotrophic biota provide a functional sink for atmospheric CO₂ (Tokoro et al., 2014).

Current global carbon budgets show a deficit that is unattributed of 0.6 Gt C yr⁻¹ (Le Quere et al., 2018). The oceanic sink of anthropogenic CO₂ for the period 2002 to 2011 is estimated at 2.5 ± 0.5 Pg C yr⁻¹ (Le Quere et al., 2013), with oceanographers researching understudied parts of the ocean, such as marginal seas and nearshore ecosystems as potential missing sinks. Bauer et al. (2013) and Borges et al. (2005) suggest (with some uncertainty) that temperate marginal seas may reduce atmospheric CO₂ by some 0.45 Pg C yr⁻¹, with nearshore wetland and estuarine ecosystems almost nullifying this sink by emitting around 0.35 to 0.40 Pg C yr⁻¹. It is suggested that future research should focus on increasing high resolution carbonate system parameter data (Mork et al., 2016) in highly productive nearshore systems, such as those containing seagrass (Borges et al., 2005; Dai et al., 2009; Jiang et al., 2011). Tidal range power schemes, such as the proposed Swansea Bay tidal lagoon^A may provide an opportunity to fabricate carbon-sequestering nearshore ecosystems that increase the potential to offset atmospheric carbon deficits.

^A <http://www.tidallagoonpower.com/projects/swansea-bay/>

Roche et al. (2016) suggest that accurate resource assessments relating to marine renewable energy (MRE) schemes are required to elucidate physical, ecological and social uncertainties when spatially refining developments to help achieve carbon reduction targets. Tidal lagoons provide an important potential resource for the MRE development mix, being both a predictable and controllable renewable energy source. The feasibility and scope of planned UK tidal lagoon energy schemes has undergone extensive examination by the 'Hendry Review'. However, uncertainty exists as to their future, given the high initial capital costs involved and possible inability to produce electricity at a competitive price. Additional benefits, such as regeneration, recreational activities and flood protection are suggested (Neill et al., 2018; NIC, 2018), however, the opportunity to incorporate carbon offsetting might also provide a second potential revenue source, increasing financial feasibility.

A naturally restricted lagoon is defined as having two or more frictional inlets, with definite tidal regimes, whereas choked lagoons characteristically have one or more long narrow inlets with greater water residence time (Kjerfve, 1986). Residence time is a quantitative measure allowing spatial and temporal estimation of the rate at which water mass ingresses and egresses a control domain. It is effectively the time taken for a particle entering the domain to leave again for the first time (Delhez et al., 2014). Ecosystem issues such as depletion in fish production have been related to limited seawater circulation and renewal (Tsihrintzis et al., 2007), because flushing has a limiting impact on nutrient input (Newton and Mudge, 2005). Salt concentration, along with nutrient and alkalinity balance may be reduced by inputs of freshwater from surface run-off, contributories, heavy and prolonged precipitation or by evaporation. It should be noted that larger lagoon systems are characteristically more stable and likely to encourage species diversity (Barnes, 1989). Ultimately, water balance, composition and quality depends on exchange at boundaries and the resultant residence time (Orfila et al., 2005; Rynne et al., 2016).

Coastal lagoons are important areas for autotrophic processes resulting in net carbon accumulation in sediments but are susceptible to anthropogenic impacts. Industrial activities such as fossil fuel combustion and cement manufacturing have increased atmospheric CO₂ concentration, influencing water pH. Terrestrial deforestation and habitat clearing have created aquatic imbalances known as cultural eutrophication and siltation, often manifested by increased turbidity, algal production, decreased light availability and dissolved oxygen levels (Kennedy and Bjork, 2009; Zouiten et al., 2013). Ultimately, this may cause loss of benthic plants and oxidation of sediments leading to net heterotrophic activity, causing the lagoon to act as a carbon source rather than a sink. It is, therefore, important to be able to robustly model carbon dynamics in order to assess whether ecosystems are CO₂ sources or sinks.

In this study, we provide a method to quantify simply and robustly mean lagoon NEP rates based on observed boundary flux estimates of DIC and modelled water exchange through the tidal channels. The study site has restricted water exchange with the open ocean through man-made inlets and is located in the vicinity of proposed sites for tidal lagoon power schemes that will follow similar water exchange regimes. As such similar regional ecosystems may provide analogous baseline study sites for proposed MRE schemes. A physical-chemical box model approach provides volumetric water exchange estimates at lateral boundaries from simulations provided by a one-dimensional (1-D) MATLAB model. Modelled hydrodynamics are well validated; thus, errors are constrained. Biogeochemical field measurements along with meteorological data allow air-sea CO₂ transfer rates to be estimated over a complete tidal cycle. This short-term study demonstrates the utility of this approach and identifies the potential for annual carbon budgeting in semi-enclosed productive coastal lagoons using high-resolution temporal data.

2. Methods

2.1 Study site

Sampling occurred in the Inland Sea (53°16.475'N, 4°35.000'W), a small (radius and surface area at low tide ~890 m and 2.5 km², respectively), shallow (~2 m at low tide), temperate, micro-tidal (<2 m range) coastal lagoon. The nearshore ecosystem is sandwiched between road and rail embankments in a channel that separates Holy Island from the island of Anglesey in Wales, UK (Figure 1). The lagoon was formed in the early 19th century when Stanley Embankment (water inlet ~17 m wide and 100 m long) was constructed to provide a transport route through to Holyhead. At the opposite end of the lagoon, Four Mile Bridge provides a much narrower road bridge and passage for water to enter (~6 m wide by 10 m long). The area is both a designated Landscape Character Area (LCA) and Area of Outstanding Natural Beauty (AONB) and provides an important well-balanced nursery and ecosystem for many different fish and marine plant species. Further detail on the area is provided by Hill (1994).

Seawater exchange with the Irish Sea occurs through the two narrow man-made inlets in the embankments. The hydrodynamic regime of the lagoon is dominated by semi-diurnal advective mixing of seawater at lateral boundaries. Periodic tidal forcing outside the basin is choked by the restricted inlets so that the tide in the Inland Sea has a lower amplitude than that of the open ocean (Hill, 1994). The lagoon supports a meadow of *Zostera noltii*, a small seagrass species of the intertidal zone of Europe and Africa (Auby and Labourg, 1996). This species exhibits strong seasonality in its above-ground biomass, ranging from 0.4 g DW m⁻² in spring to 70 g DW m⁻² in summer (Papadimitriou et al., 2006). There are a number of proposed MRE

developments for this region, including a tidal range lagoon scheme to the east at Colwyn Bay (Roche et al., 2016).

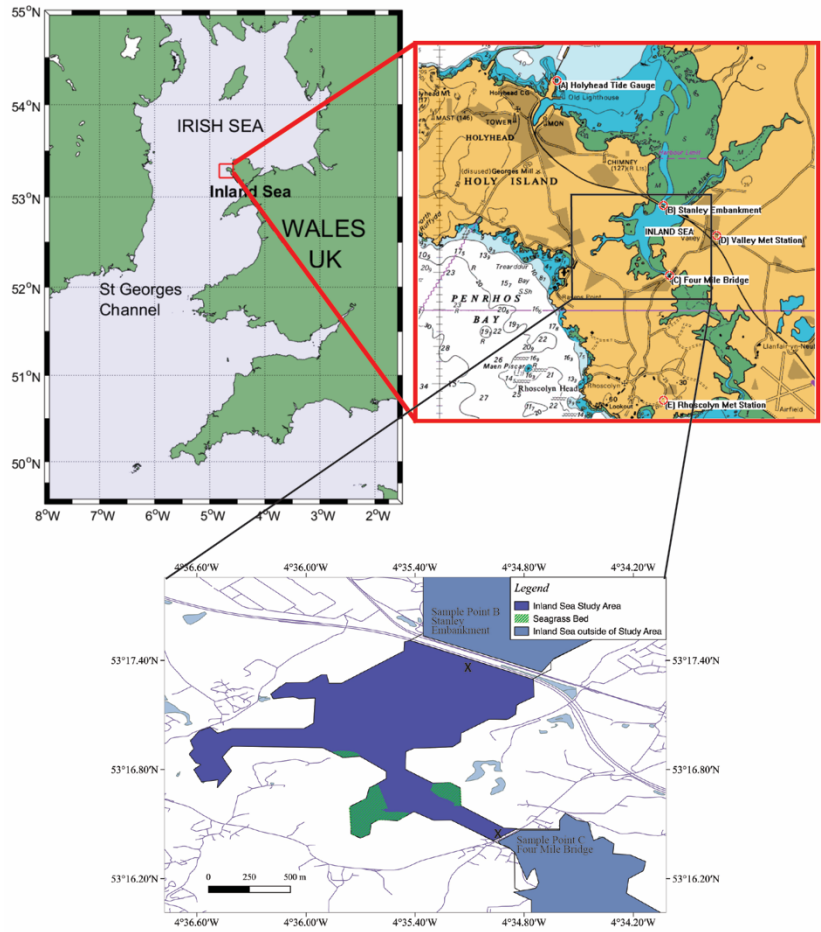


Figure 1. Location of the Inland Sea showing the restricted channels to the north at Stanley Embankment (B) and to the south at Four Mile Bridge (C). Modelled boundary conditions are based on data supplied by Holyhead harbour primary tide gauge station (A) and meteorological data is taken from stations at Valley (D) and Rhoscolyn (E).

2.2 Biogeochemical model

A simple theoretical 1-D biogeochemical model, adapted from Jiang et al. (2011) (Figure 2) is used to examine the extent to which lagoon DIC concentration is influenced by CO₂ gas exchange caused by a combination of:

- (i) air-sea exchange (surface boundary)
- (ii) physical mixing (lateral boundary)
- (iii) biological influences (seabed and water column)

DIC determination is outlined in section 2.4. We apply the fundamental principles of a tracer (in this case DIC) entering and exiting a semi-enclosed system and assume (a) lagoon volume is conserved and (b) a fully mixed water column. Therefore, tracer concentration (c , in mmol C kg⁻¹) in a varying water depth over time is given by eq (1) (Williams and Fellows, 2011):

165

$$\frac{d}{dt} \rho c \frac{V}{A_S} = \sum F_{out} - F_{in} = F_{MIX} - F_{GAS} - F_{BIO} \quad (1)$$

166

167 In the above equation, ρ is water density (kg m^{-3}), V system volume (m^3), A_S surface
 168 area (m^2), and F is the tracer flux ($\text{mmol C m}^{-2} \text{ hr}^{-1}$) entering (F_{in}) and exiting (F_{out}) the
 169 system at the boundaries. DIC fluxes in and out of the lagoon can further be expressed
 170 as the sum of the partial fluxes generated by a number of biogeochemical processes
 171 within the lagoon:

- 172 (i) Physical mixing during transport by advection over ebb and flood tidal cycles,
 173 riverine input, and upwelling (F_{MIX}).
 174 (ii) Ecosystem respiration, adding respired organic carbon as CO_2 to the water,
 175 and ecosystem production removing DIC species (aqueous CO_2 , bicarbonate
 176 ions) from the water into biomass and calcium carbonate (CaCO_3) precipitation
 177 and dissolution, combined as F_{BIO} .
 178 (iii) Air-sea exchange of CO_2 (F_{GAS}). If $F_{in} > F_{out}$, there will be a net increase in DIC
 179 concentration in the lagoon water, and vice versa.

180

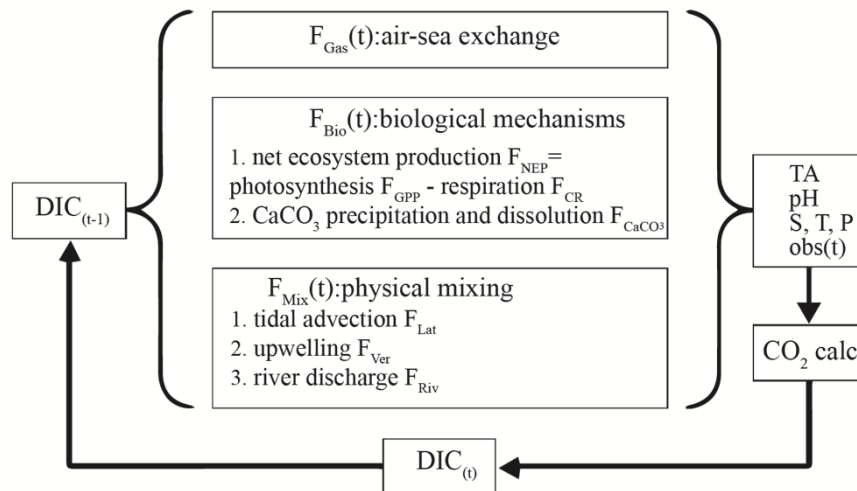


Figure 2. Biogeochemical 1-D model of carbonate system exchange dynamics when accounting for associated air-sea gas exchange, biological activity and physical processes in a nearshore shallow water ecosystem.

181

182 2.2.1 Biological processes

183 We simplify the approach to carbon dynamics in the lagoon by considering a
 184 semi-enclosed system (Figure 3). At first approximation, we assume that the
 185 contribution from CaCO_3 precipitation and dissolution is negligible (Barron et al., 2006).
 186 Based on eq (1), at steady state F_{BIO} is equivalent to NEP, the balance between gross
 187 primary production and community respiration, $F_{BIO} = \text{NEP} = \text{GPP} + \text{CR}$. By

convention, the transfer of carbon from atmosphere to seawater and lagoon to ocean due to respiration have negative values.

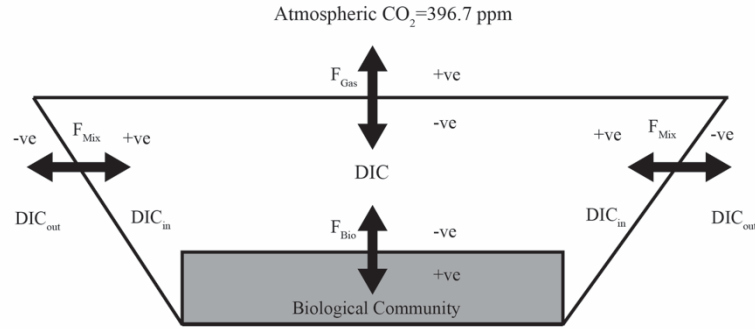


Figure 3. Schematic box model of the Inland Sea and its perceived inorganic carbon exchange. Lateral tidal mixing (Mix), biological (Bio) and gas (Gas) exchanges will drive net DIC concentration levels within the lagoon.

2.2.2 Air-sea exchange

In this study, we determine F_{GAS} with the bulk formula method as $F_{GAS} = \alpha k \Delta p CO_2$. Where α is the solubility coefficient of CO_2 ($mmol\ m^{-3}\ \mu atm^{-1}$), k is gas transfer velocity ($m\ hr^{-1}$; a function of wind speed) and $\Delta p CO_2 = pCO_{2W} - pCO_{2A}$ (μatm), the air-sea difference in the partial pressure of CO_2 . Subscripts W and A refer to water and atmosphere respectively.

2.2.3 Physical mixing

By observing any two of the four measurable carbonate system parameters, pH, DIC, total alkalinity (TA) and pCO_2 , along with water temperature and salinity, it is possible to determine the remaining parameters. In this study, DIC in lagoon water is determined from field observations of pH and TA at lateral boundaries. The physical processes of tidal advection, upwelling, and river discharge contribute to DIC mixing at ecosystem boundaries. Advection of nutrients from ocean tides dominate the Inland Sea, no other significant contributories exist. The tidal exchange of water through the man-made inlets provides fluxes calculated from the product of volumetric flow throughput, U ($m^3\ hr^{-1}$) and water density. The mixing of lagoon and ocean water includes tracer concentration, such that $F_{MIX} = c_L \rho U_{out} - c_O \rho U_{in}$ whereby subscripts *in* and *out* describe exchange on flood and ebb tides and subscripts *L* and *O* indicate lagoon and ocean concentrations, respectively.

2.3 Hydrodynamic model

The hydrodynamic model provides a means to estimate volumetric channel throughput, U . Following Hill (1994), the tide in the Inland Sea is modelled by

considering the balance between the pressure gradient force caused by the slope of the water surface and bottom friction:

$$g \frac{\eta_o - \eta_L}{L} = k_D \frac{u^2}{H + \eta_m} \quad (2)$$

Where g is the gravitational acceleration constant (9.81 m s^{-2}), η_o is surface elevation relative to mean sea level in the open sea (m), and η_L is surface elevation relative to mean sea level in the lagoon (m). The depth-averaged along-channel current velocity u (m s^{-1} , positive when flow is into the lagoon), and k_D the dimensionless drag coefficient in a channel of length L and depth H below mean sea level (m). Mean surface elevation in the channel is denoted by $\eta_m = (\eta_o + \eta_L) / 2$. The continuity equation is:

$$A_S \frac{d\eta_L}{dt} = ub(H + \eta_m) \quad (3)$$

and we consider ideal channels of width b (m), whose cross section does not alter. Crucially, however, in addition we allow the surface area of the lagoon to change with the tide, assuming the lagoon has sloping sides and a conical shape. If the sides slope at an angle θ ($^\circ$) to the horizontal, the surface area of the lagoon varies with elevation according to:

$$A_S = \pi \left(r_0 + \frac{\eta_L}{\tan \theta} \right)^2 \quad (4)$$

The subtidal lagoon radius, r_0 (m) is that at lowest-tide, assumed constant with depth beyond this.

Tidal forcing in the open sea can be represented by a sum of harmonics:

$$\eta_o = \sum_{n=1}^N a_n \cos(\omega_n t - \kappa_n) \quad (5)$$

Where a_n and κ_n are the amplitude (m) and phase ($^\circ$) of n (1-N) tidal constituents with an angular frequency $\omega_n = \frac{2\pi}{T_n}$ with T_n being the period (s) of the constituent. For this study, twelve of the main harmonic constituents are used to represent surface elevation change due to astronomical forcing. Tidal boundary forcing at the Inland Sea

is assumed to occur at the same phase and amplitude as that at Holyhead harbour (A in Figure 1). The flow in the channels is derived by solving eq (2) for u and then using eq (3) to update the elevation in the Inland Sea. The equations are solved using a thirty-second-time step with meteorological influences neglected. U is derived from the product of channel flow velocity and cross-sectional area, which varies with depth over time.

2.4 Water residence time and NEP

Water exchange and mixing through the channels will not occur instantly and concentrations due to mixing will alter slowly and be affected by a proportion of water returning into the domain soon after leaving. Therefore, the average residence time of the water must be factored into calculations. In order to account for this mixing process, we approach the problem using the tracer pulse method that associates the residence time (T) of a system (in this case the lagoon basin) with n measured tracer flux concentration observations (F_{tr}) at any given point on the periphery during an elapsed time (t) by means of the transport equation:

$$T = \frac{\sum_{n=0}^{\infty} F_{tr} t}{\sum_{n=0}^{\infty} F_{tr}} \quad (6)$$

We solve the steady state condition of eq (6) by integrating over time the multiple tracer DIC flux observations to reveal the solution to tracer transport for a time step equal to a tidal cycle:

$$NEP = \frac{1}{T_{TC}} \int_0^{TC} F_{MIX} - F_{GAS} dt \quad (7)$$

Water residence time during a tidal cycle (T_{TC}) is the ratio of the mean volume of the lagoon V_L , (m^3) to the tidal prism volume, V_{TP} , ($m^3 \text{ hr}^{-1}$) which is the difference between high and low tide volumes or throughput in the channel(s) over an ebb tide (Sheldon and Alber, 2006). For an implicit timescale of a tidal cycle, V_{TP} represents the volume change or throughput over the tidal period, T_{TC} .

$$T_{TC} = \frac{V_L}{V_{TP}} = \frac{\bar{V}}{\Delta V / T_{TC}} \quad (8)$$

In the above equation, the overbar represents the integrated mean values of the polynomial curve fit. We assume negligible difference in concentration values at each lagoon entrance at all times.

3. Applied theory

3.1 Measurements and Analysis

Sampling was conducted in surface waters in daylight hours during an ebb tide pilot study on 1 August 2013 (JD 213) and over a complete tidal cycle during spring tide on 20 August 2013 (JD 232) within a 20 m radius of the culvert entrances at Four Mile Bridge and Stanley Embankment (Figure 1). No precipitation occurred during this time. Single-point current velocity measurements were taken in triplicate at 10- or 15-minute intervals at channel inlets during ebb tides throughout July and August using a Braystoke BFM002 miniature current flow meter. Combined half hour moving averages of these measurements were used to validate model estimates (section 3.2). Solar irradiance was determined from hourly moving averages of data supplied by the observatory at Hilbre Island (53°22.980'N, 3°13.680'W) and is used to support evidence of thermal changes in the lagoon.

The seawater DIC concentration, partial pressure of CO₂ in seawater ($p\text{CO}_{2\text{W}}$) and hence the air-sea CO₂ transfer rate (F_{GAS}), were all computed from temperature, practical salinity, TA, and pH measurements using CO2Calc version 1.2.0 (Robbins et al., 2010). Parameters were determined by setting the seawater pH scale using the Dickson and Millero (1987) re-fit of the Mehrbach et al. (1973) stoichiometric dissociation constants of dissolved CO₂, the stoichiometric dissociation constant of HSO₄⁻ (K_{HSO_4}) in Dickson (1990), the total boron concentration in Lee et al. (2010) and air-sea transfer rate parameters of Wanninkhof (1992). Combined hourly moving averages of wind velocity data provided from meteorological stations at Valley (53°16.980'N, 4°33.780'W, 9 m elevation) and Rhoscolyn (53°14.760'N, 4°34.980'W, 13 m elevation) on Anglesey were included to calculate gas transfer velocity (k), in order to estimate the air-sea CO₂ flux also (section 2.2.2). The global average for atmospheric CO₂ concentration (396.7 ppm, NOAA, 2013) was utilized in all calculations of the air-sea $p\text{CO}_2$ gradient necessary for the computation of the air-sea CO₂ transfer rate, as local values are not available nor were in-situ values recorded.

Salinity was measured in sub-samples in the laboratory at ambient temperature (18 - 22°C) using a portable conductivity meter (WTW Cond 3110) with a WTW Tetracon 325 probe. TA was determined within four days of collection from refrigerated, unfiltered, un-poisoned seawater samples stored in 500 mL borosilicate bottles with ground-glass stoppers sealed with vacuum grease (Apiezon M). The TA

analysis was conducted by potentiometric titration with HCl of sample aliquots of known weight at constant temperature in a jacketed vessel using a Metrohm Titrando 888 unit. The automatic burette, pH meter, Pt temperature probe, Ag/AgCl/KCl reference electrode, and glass electrode were calibrated with buffers traceable to SRM from NIST and PTB (Merck, pH 2.00, 4.01, 7.00, 9.00 and 10.00 at 25°C). Daily duplicate potentiometric titrations of CRMs yielded $2227.70 \pm 0.68 \mu\text{mol kg}^{-1}$ for Batch #102 ($n = 19$, certified TA = $2227.46 \pm 0.67 \mu\text{mol kg}^{-1}$) and $2221.22 \pm 1.44 \mu\text{mol kg}^{-1}$ for Batch #112 ($n = 6$, certified TA = $2223.26 \pm 0.89 \mu\text{mol kg}^{-1}$). The coefficient of variation as relative standard deviation for TA was better than 0.2%.

A combined glass electrode and temperature probe (Inlab, 0.1°C resolution) coupled to a portable Mettler Toledo SG2 (MT+2) pH meter were used for seawater temperature and pH measurements. The Inlab combination electrode was calibrated using the buffers described above in a jacketed vessel at constant temperature every 2°C from 5 to 20°C and at 25°C. Linear regression of electrode-buffer potential E (in mV) versus NIST buffer pH yielded the electrode-specific apparent standard potential (E_o) and potentiometric slope as a function of temperature (Figure 4a). The potentiometric slope deviated by 1.2% from ideal electrochemical behavior as expressed by the Nernst slope in the temperature range of 10 to 25°C.

The E_o and potentiometric slope temperature functions were used to compute seawater pH on the NIST scale from the in-situ electrode-seawater E and temperature measured at 15-minute intervals by immersing the electrode in the main water mass for a period of no less than 120 s. The MT+2 pH meter offered 1 mV resolution, equivalent to 0.02 pH unit measurement uncertainty. The seawater pH on the seawater scale (pH_{SWS}) was determined from pH_{NIST} as $\text{pH}_{\text{SWS}} = \text{pH}_{\text{NIST}} + \log(f_{\text{H}^+})$, with f_{H^+} equal to the apparent proton activity coefficient determined at the in-situ salinity as a function of temperature by potentiometric titration (outlined above) as described in Gleitz et al. (1995). For this purpose, the Inlab electrode was coupled to the Metrohm titration system, and Inland Sea water was titrated for TA in triplicate every 5°C from 10°C to 25°C. The f_{H^+} exhibited a linear temperature dependency at $S = 34.9$ of the seawater sample (Figure 4b).

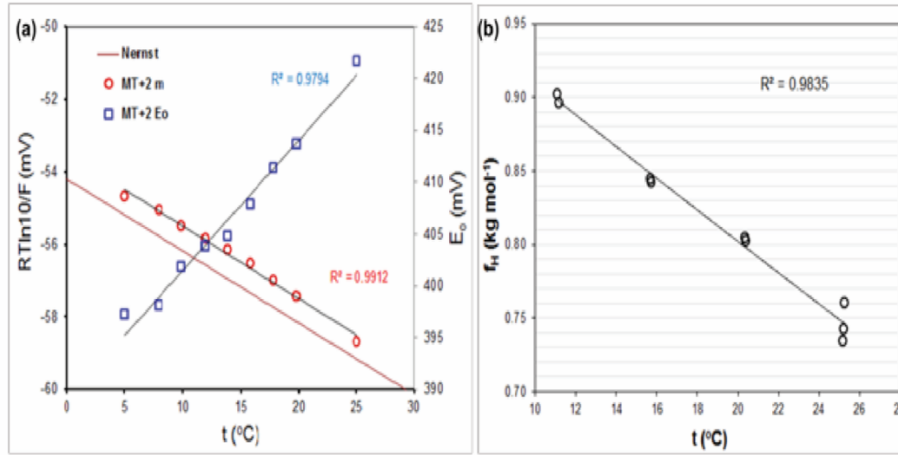


Figure 4. (a) Measured and ideal (Nernst) potentiometric slope ($RT \ln 10 / F$) and apparent standard potential (E_o) as a function of temperature of the Mettler Toledo Inlab combination pH-temperature probe using NIST buffer solutions. (b) Apparent proton activity coefficient (f_{H+}) as a function of temperature at $S = 34.9$ in seawater. The straight lines through the data represent linear regression fits.

3.2 Hydrodynamic model validation

Thirty-minute moving averages of single point flow measurements during ebb tide through both channels of the Inland Sea compare well against model outputs (Figure 5). Mean (± 1 s.d) channel velocities of 1.65 ± 0.10 m s $^{-1}$ ($n = 14$), 1.74 ± 0.18 m s $^{-1}$ ($n = 11$), and 1.02 ± 0.04 m s $^{-1}$ ($n = 10$) were recorded using the flow meter on 17 July 2013 (JD 198), 19 July 2013 (JD 200), and 1 August 2013 (JD 213), respectively. Simulated model outputs for the same periods provided 1.37 ± 0.12 m s $^{-1}$ ($n = 64$), 1.66 ± 0.06 m s $^{-1}$ ($n = 45$), and 1.05 ± 0.05 m s $^{-1}$ ($n = 44$).

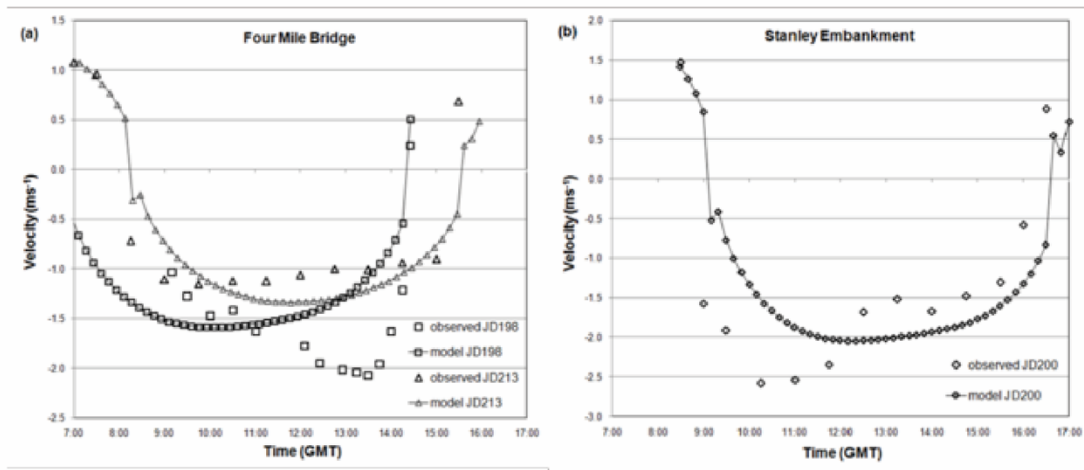


Figure 5. Modelled and observed channel currents. Negative values denote water ebbing away from the lagoon as it empties. Observations were made at culvert entrances to the lagoon at (a) Four Mile Bridge and (b) Stanley Embankment.

Modelled boundary tidal forcing, expressed as ocean elevation and phase change at Holyhead (degrees converted to decimal days to provide comparison continuity) for 1 July 2013 (JD 182) to 31 August 2013 (JD 243) inclusive are compared to values published by EasyTide, having decimeter resolution (Figure 6). Mean (± 1 s.d) variation in modelled ocean surface elevation above chart datum (ACD) against published values is 9.5 ± 0.4 cm and the mean variation in phase $1.74^\circ \pm 0.07^\circ$ equivalent to $0.06 \pm 2.4 \times 10^{-3}$ hr ($n = 239$). Field observations of high and low water times within the Inland Sea are used to validate modelled lagoon phase dynamics (Table 1). These compare well to model predictions; the mean deviation of the modelled lagoon phase is $3.06^\circ \pm 2.50^\circ$ or 0.11 ± 0.09 hr ($n = 9$). Tidal range within the lagoon was also recorded on various days during the study, these observations deviated from modelled lagoon elevation by 2.0 ± 0.7 cm ($n = 4$). Modelled lagoon surface area minimum and maximum values of 2.43 km^2 and 6.50 km^2 were estimated for the period.

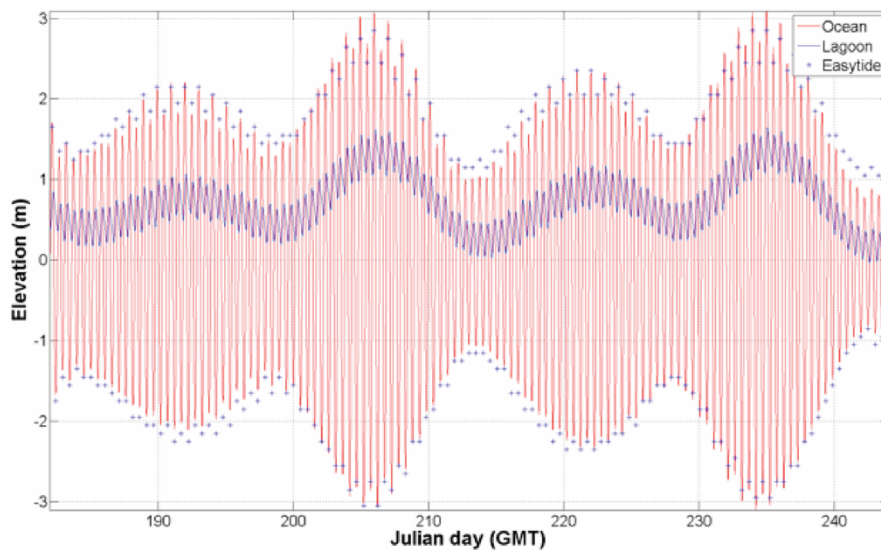


Figure 6. Modelled boundary forcing (red line) based on tidal harmonics at Holyhead compared to published EasyTide data (blue crosses). Simulated lagoon elevation change (blue line) is also plotted.

Table 1 Observations of lagoon high and low water times used to validate modelled lagoon tidal phase and range.

Lagoon tidal phase (hh:mm GMT)		
observed	model	error
JD192 09:37	09:45	+00:08
JD198 14:20	14:12	-00:08
JD200 08:47	08:49	+00:02
JD200 16:15	16:26	+00:11
JD213 07:56	07:59	+00:03
JD213 15:19	15:20	+00:01

JD232 06:57	07:02	+00:05
JD232 11:25	11:23	-00:02
JD232 18:52	19:09	+00:17

Lagoon tidal range (m)

JD200 0.45	0.46	+0.01
JD213 0.42	0.43	+0.01
JD232 0.49	0.47	-0.02
JD232 0.46	0.50	+0.04

4. Results

Mass balance of DIC is controlled by a combination of physical and biological processes. These include temperature change, water mixing, photosynthetic production of organic material, respiration of marine biota, calcium carbonate precipitation and dissolution, and air-sea transfer of CO₂ across the surface boundary layer. Photosynthesis, CaCO₃ precipitation and CO₂ evasion all consume DIC, while respiration, CaCO₃ dissolution and CO₂ transfer from atmosphere recycle carbon back into the DIC pool from the organic, mineral and gaseous phases, respectively (Papadimitriou et al., 2012). An imbalance, therefore, in the sinks and sources of DIC will result in a net change in the DIC concentration in an aquatic system.

During these processes, the marine CO₂ system will re-equilibrate, with consequent changes in parameters such as pH and the $p\text{CO}_{2W}$ of the system. The change in DIC concentrations derived from the empirical observations in this study are considered to be the result of influence from some, or all, of the processes of gas exchange, advection and net ecosystem productivity, leading to a net deficit or excess in the balance between fluxes entering and leaving the lagoon. By capturing the carbon exchange rate at ecosystem boundaries, overall assessment of the net balance between these processes is achieved. Our resultant analysis indicates whether the ecosystem acts to balance the carbon budget as a net sink or source during the study period.

4.1 Lagoon system

Changes in lagoon water parameters were observed from 08.00 to 19.30 BST, during a complete spring tidal cycle. The mean lagoon water residence time is estimated at 39 ± 6 hr calculated from simulated model channel throughput values (Table 2). Seawater temperature increased linearly from 16.6°C to 19.8°C over the course of the day, reaching a plateau during mid-afternoon while salinity remained relatively constant at 34.01 ± 0.02 (± 1 s.d, $n = 24$). During the flood period, the pH_{sws} varied between 8.05 and 8.13, while during the ebb tide it increased systematically from 8.05 to 8.26. Total alkalinity initially decreased during flood tide from 2329 $\mu\text{mol kg}^{-1}$ to 2300 $\mu\text{mol kg}^{-1}$ and remained relatively constant for most of the ebb tide, with a

small step change of $\sim 10 \mu\text{mol kg}^{-1}$ toward the end of the study period. The calculated DIC and $p\text{CO}_{2\text{W}}$ exhibited similar behaviour with sinusoidal fluctuations. During the flood tide, the DIC exhibited a short initial increase followed by a sustained systematic decrease from 2092 to 1937 $\mu\text{mol kg}^{-1}$. Over the same period, the $p\text{CO}_{2\text{W}}$ fluctuated between 312 μatm and 394 μatm during flood and exhibited a systematic decrease from 330 μatm to 220 μatm during ebb (Figures 7 and 8; Table 3).

The $p\text{CO}_{2\text{W}}$ indicates that, throughout the study period, CO_2 levels in the lagoon were conducive to transfer of CO_2 from the atmosphere to seawater. Wind velocity increased over the course of the day from 1.6 m s^{-1} at the start of the study to almost 5 m s^{-1} by the end (Figure 8). The F_{GAS} calculations were estimated to be negative throughout the study period (Figure 9), indicating again that the air-sea exchange of CO_2 occurred from atmosphere to seawater. There was an increase from a minimum air-sea flux of $-0.002 \text{ mmol C m}^{-2} \text{ hr}^{-1}$ to a maximum of $-0.38 \text{ mmol C m}^{-2} \text{ hr}^{-1}$, with a mean ($\pm 1 \text{ s.d.}$) $F_{\text{GAS}} = -0.13 \pm 0.26 \text{ mmol m}^{-2} \text{ hr}^{-1}$. The mean NEP rate for this tidal period is estimated at $3.0 \pm 0.4 \text{ mmol C m}^{-2} \text{ hr}^{-1}$ (Table 3), with F_{GAS} equivalent to 4.3% of NEP DIC provision.

Table 2 Calculated water residence time based on cumulative modeled channel flow data over the mean ebb and flood period during sampling.

	Flood ($\text{m}^3 \text{ hr}^{-1}$)	Ebb ($\text{m}^3 \text{ hr}^{-1}$)	Water Residence Time (hr)
Min	3032258	1098513	33.4
Max	3057142	823390	45.0
Mean Period (hr)	4.5	7.6	

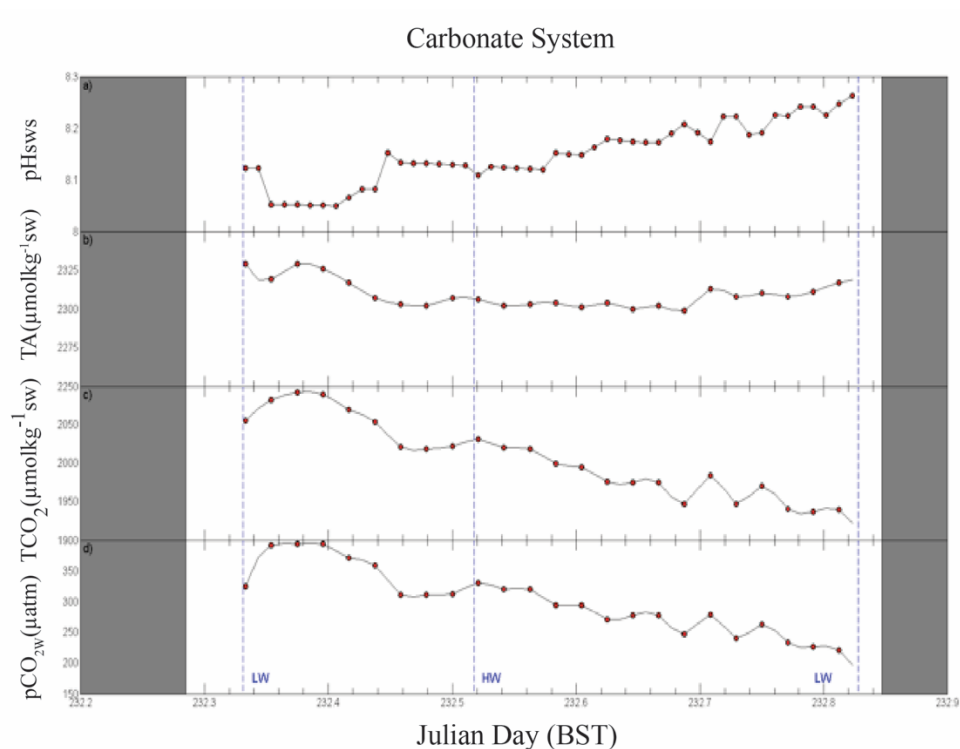


Figure 7. Lagoon carbonate system parameters of (a) pH (b) TA (c) DIC and (d) $p\text{CO}_2$ on JD 232 (solid markers). DIC and $p\text{CO}_2$ are derived from CO2Calc estimates of in-situ pH and TA observations. High and low water (blue lines) and non-daylight hours (grey areas) are also indicated.

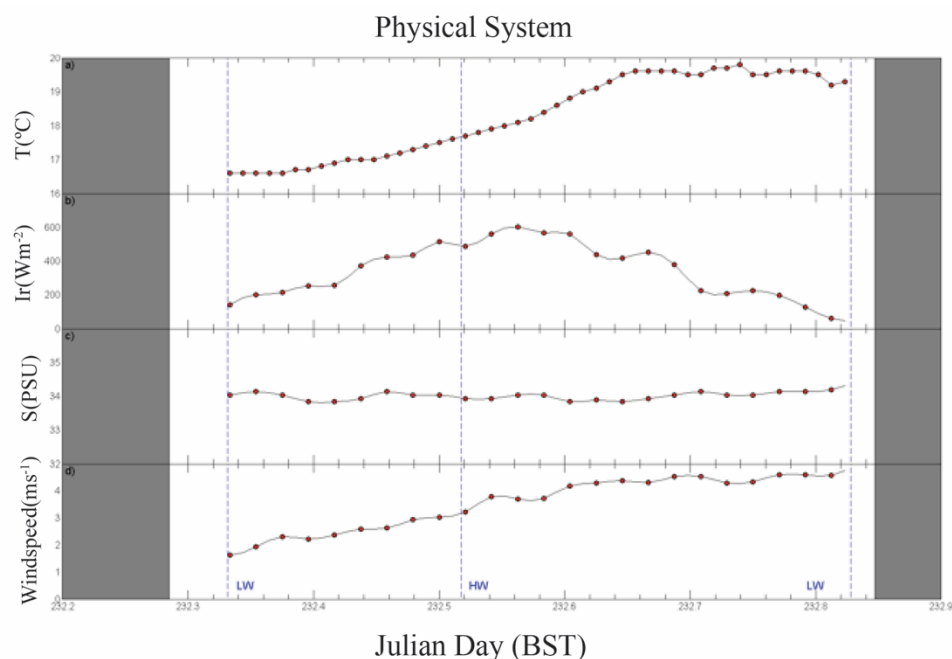


Figure 8. Lagoon physical parameters of (a) water temperature (b) surface solar irradiance (c) salinity (d) and surface wind speed observed on JD 232. High and low water (blue lines) and non-daylight hours (grey areas) are also indicated.

Table 3 Measured seawater salinity, temperature, pH and TA along with calculated DIC, $p\text{CO}_2$, and air-sea CO_2 exchange rate (F_{GAS}) in the Inland Sea. The NEP value is the overall estimated daytime average. A net carbon sink is inferred from a positive NEP value and a negative F_{GAS} indicates a net transfer of CO_2 from the atmosphere to seawater. The mean water residence

431 time was derived from a validated 1-D MATLAB model of boundary volumetric flow, while DIC
 432 ($\pm 8 \mu\text{mol kg}^{-1}$) and $p\text{CO}_2$ ($\pm 20 \mu\text{atm}$) were derived from CO2Calc.
 433

NEP								Mean Water Residence Time							
(mmol C m ⁻² hr ⁻¹)								(hr)							
3.0 ± 0.4								39 ± 6							
Time (BST)	Salinity		Temp (°C)		pH _{sws}		TA		DIC		pCO ₂		F _{GAS}		
							(μmol kg ⁻¹)	(μmol kg ⁻¹)	(μatm)	(mmol C m ⁻² hr ⁻¹)					
	JD213	JD232	JD213	JD232	JD213	JD232	JD213	JD232	JD213	JD232	JD213	JD232	JD213	JD232	
08:00	33.3	34.0	17.5	16.6	8.04	8.12	2323	2329	2089	2055	406	325	0.022	-0.020	
08:30	33.4	34.1	17.5	16.6	8.04	8.05	2323	2319	2089	2082	405	391	0.020	-0.002	
09:00	33.4	34.0	17.5	16.6	8.04	8.05	2326	2329	2092	2092	406	394	0.016	-0.002	
09:30	33.5	33.8	17.5	16.7	8.04	8.05	2325	2326	2090	2090	405	394	0.017	-0.002	
10:00	33.4	33.8	17.5	16.9	8.04	8.07	2330	2317	2095	2070	407	371	0.022	-0.015	
10:30	33.0	33.9	17.6	17.0	8.04	8.08	2333	2307	2100	2054	409	359	0.020	-0.026	
11:00	33.3	34.1	17.8	17.1	8.06	8.13	2333	2303	2082	2020	385	312	-0.017	-0.061	
11:30	33.3	34.0	18.0	17.3	8.09	8.13	2331	2302	2067	2019	355	312	-0.054	-0.076	
12:00	33.3	34.0	18.3	17.5	8.08	8.13	2327	2307	2064	2021	364	312	-0.040	-0.080	
12:30	33.5	33.9	18.7	17.7	8.08	8.11	2316	2306	2051	2031	362	330	-0.044	-0.072	
13:00	33.6	33.9	19.1	17.9	8.11	8.12	2308	2302	2023	2020	331	321	-0.083	-0.113	
13:30	33.6	34.0	19.6	18.1	8.12	8.12	2309	2303	2014	2018	322	320	-0.081	-0.109	
14:00	33.6	34.0	19.9	18.4	8.12	8.15	2310	2304	2012	1999	322	294	-0.086	-0.147	
14:30	33.6	33.8	20.2	18.8	8.13	8.15	2314	2301	2007	1994	313	294	-0.093	-0.185	
15:00	33.4	33.9	20.5	19.1	8.16	8.18	2317	2304	1988	1976	288	270	-0.121	-0.242	
15:30	33.6	33.8	20.5	19.5	8.16	8.17	2319	2300	1991	1975	288	277	-0.090	-0.236	
16:00	33.6	33.9	20.7	19.6	8.21	8.17	2322	2302	1955	1975	249	277	-0.166	-0.229	
16:30	33.7	34.0	20.3	19.6	8.18	8.21	2317	2299	1973	1946	271	246	-0.143	-0.318	
17:00		34.1		19.5		8.17		2313		1984		278		-0.251	
17:30		34.0		19.7		8.22		2308		1947		240		-0.298	
18:00		34.0		19.5		8.19		2310		1970		263		-0.260	
18:30		34.1		19.6		8.23		2308		1941		233		-0.357	
19:00		34.1		19.6		8.24		2311		1937		227		-0.369	
19:30		34.2		19.2		8.25		2317		1939		221		-0.380	

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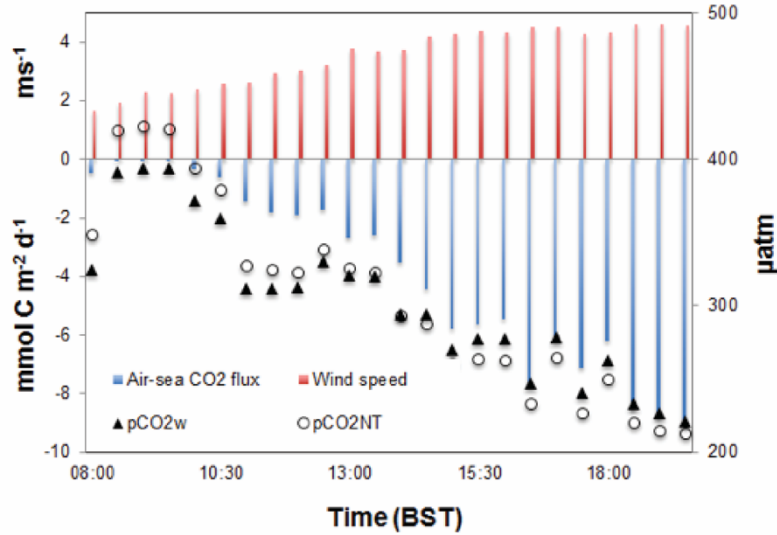


Figure 9. Air-sea CO₂ exchange, wind velocity, $p\text{CO}_{2W}$ and temperature normalized partial pressure of CO₂, $p\text{CO}_{2,NT}$ for the study period on JD 232. Outgassing inferred from $p\text{CO}_{2,NT}$ values early in the study period is prevented by low water temperature that increases gas solubility and lowers $p\text{CO}_{2W}$ preventing transfer of CO₂ from lagoon to atmosphere.

5. Discussion

5.1 Thermal effects

Temperature change affects the solubility of CO₂ in water, whereby an increase in temperature by 1°C causes approximately 4% $p\text{CO}_{2W}$ increase as the dissolved gas dissociates (Gazeau et al., 2005; Jiang et al., 2011; De Carlo et al., 2013). Using CO2Calc to assess the maximum possible change of $p\text{CO}_{2W}$ ($\Delta p\text{CO}_{2,T}$) from the temperature variation observed over the full tidal cycle on JD232 by fixing DIC and TA values at the lowest observed diel temperature and allowing pH to vary with inputs of minimum and maximum recorded temperature, we found that $\Delta p\text{CO}_{2,T} = 46 \mu\text{atm}$. This is the maximum extent to which the temperature change within the lagoon can affect the $p\text{CO}_{2W}$ of the system ($p\text{CO}_{2,T}$) during the study period. This value was confirmed by isolating the thermally forced $p\text{CO}_{2W}$ changes to reveal only the change due to $p\text{CO}_{2,T}$ using the approach of Takahashi et al. (1993).

$$p\text{CO}_{2,T} = p\text{CO}_{2,\text{mean}} \times e^{0.0423 \times (T_{\text{obs}} - T_{\text{mean}})} \quad (9)$$

Here $p\text{CO}_{2,T}$ and $p\text{CO}_{2,\text{mean}}$ are the $p\text{CO}_{2W}$ values from thermal forcing alone and the in-situ average, respectively, while T_{mean} and T_{obs} are the in-situ mean and observed water temperature, respectively. This thermally isolated change reveals a similar 40 μatm change for the 3.2°C temperature increase observed in the lagoon water, resulting in only a 3.8% difference in value.

A maximum diel range in $p\text{CO}_{2\text{W}}$ of approximately 172 μatm as observed on JD 232 (Figure 9) can be attributed to a combination of the remaining physical and biogeochemical processes within the lagoon, which have over three times the influence that temperature effects alone can explain. We used a similar approach in order to isolate the influences of the non-thermal processes of mixing, gas exchange and biological activity from the temperature effect on $p\text{CO}_{2\text{W}}$ by normalizing to the mean temperature during empirical observations ($p\text{CO}_{2,\text{NT}}$) using the following formula:

$$p\text{CO}_{2,\text{NT}} = p\text{CO}_{2,\text{Tobs}} \times e^{0.0423 \times (T_{\text{mean}} - T_{\text{obs}})} \quad (10)$$

where $p\text{CO}_{2,\text{NT}}$ and $p\text{CO}_{2,\text{Tobs}}$ are the $p\text{CO}_{2\text{W}}$ values from temperature normalized and actual observation calculations, respectively. The normalized values along with $p\text{CO}_{2\text{W}}$ can be compared to reveal the time-based influence of temperature on the system.

The relative importance of thermal contribution over the course of the study period is highlighted by the lower temperatures in the lagoon at the start of the study due to low solar irradiance and the influence of incoming seawater. These factors promote greater solubility of CO_2 and act to prevent the system from outgassing to atmosphere during this time. As the day progresses and the absorbed radiant energy peaks, the thermal contribution predictably acts to increase $p\text{CO}_{2\text{W}}$. Given an assumed constant $p\text{CO}_{2\text{A}}$ (396.7 ppm, NOAA, 2013), the air-sea flux drives CO_2 into the water column due to the increasing $p\text{CO}_2$ gradient, aided by an increase in wind velocity as the study period progressed, thus promoting aquatic CO_2 uptake (Takahashi et al., 2002). It should also be noted that the influence of processes acting to reduce $p\text{CO}_{2\text{W}}$ appear to have greater impact in the lagoon than that of air-sea exchange influenced by wind speed (Figure 9).

Using CO2Calc (section 3.1) we compute pH_{25} from the recorded salinity, TA and DIC values (Table 3) and compare this with the in-situ pH data. As temperature has a significant impact on this parameter, the temperature corrected value highlights the biological influence in the signal. The corrected 25°C value is warmer than in-situ measurements, therefore we expect to see lower pH_{25} values. A clear reduction in the signal difference over time can be seen in Figure 10 as the lagoon system warms. The difference in the two pH values has a scale corrected range from 88.0% (08.30 to 09.00) to 93.4% (17.30) that can be attributed to biological activity alone.

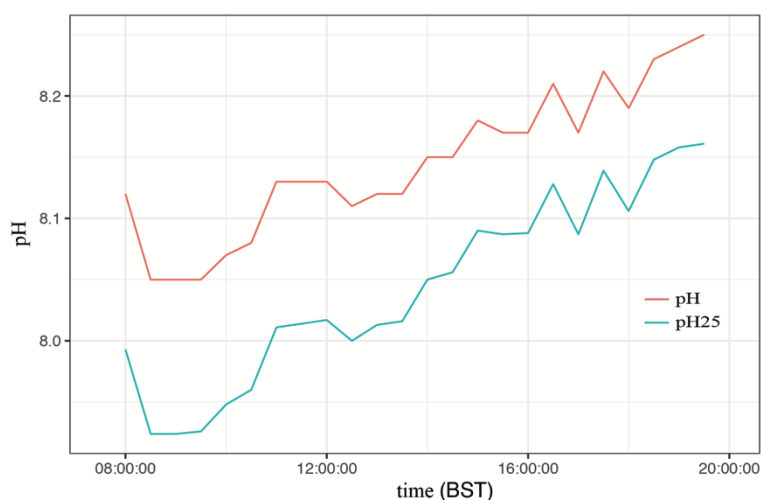


Figure 10. The pH₂₅ was computed using CO2SYS from measured salinity, TA, and DIC values (Table 3), using a constant temperature of 25°C.

5.2 Biogeochemical effects

Using the stoichiometry of potential contributing biogeochemical processes that could affect the CO₂ system of the lagoon, the fractional contribution of each to the TA-DIC mass balance can be assessed. This is achieved by examining the distribution of salinity-normalized values of lagoon TA against DIC concentration relative to the equivalent incoming seawater concentration from outside the basin. Photosynthesis will cause a slight increase in TA due to nutrient uptake and will reduce the DIC concentration due to its uptake by primary producers within the system, whereas respiration will have the opposite effect. Both processes result in a low ratio of TA to DIC concentration change, with $\Delta A_T : \Delta C_T = -0.16$ (Lazar and Loya, 1991; Wolf-Gladrow et al., 2007). The ratio of TA to DIC concentration change during calcification and CaCO₃ dissolution is 2, while for benthic anaerobic respiration via sulphate reduction with sulphide accumulation in sediment pore waters, $\Delta A_T : \Delta C_T = 1$ (Wang & Cai 2004; Wolf-Gladrow et al., 2007; Soetaert et al., 2007; Zhai et al., 2017).

The dominance of each of these processes to the biogeochemistry of the lagoon depends on a number of factors and could be overridden by external forces, such as freshwater input, lagoon stratification, and water residence time (Gupta et al., 2008; Kone et al., 2009; Muduli et al., 2012; Zhai et al., 2017). Their magnitude and seasonal variability will affect the biogeochemistry of the lagoon and the net air-sea CO₂ exchange. The trend in the current salinity-normalized TA versus DIC data over the study period suggests that the carbonate system in the lagoon at full insolation was influenced by photosynthesis and CO₂ transfer from the atmosphere (Figure 11). The sustained increase of pH with temperature and stable TA throughout the heightened solar period, combined with an increased air-sea flux gradient suggests that maximum utilization of CO₂ occurs within the lagoon. Some moderate fluctuation in the normally conservative TA parameter (Figure 7) suggests that it was affected somehow during

the study, but no water mass mixing occurs and CaCO_3 precipitation-dissolution appears to be negligible as a $\Delta A_T : \Delta C_T = 2$ in the salinity-normalized values would be expected (Figure 11).

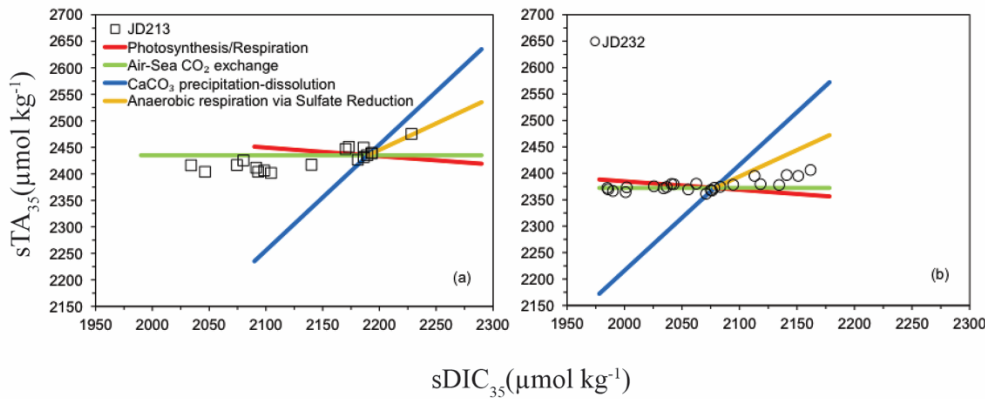


Figure 11. TA versus DIC concentrations in lagoon water observed during (a) JD 213 and (b) JD 232 normalized to $S = 35$, plotted relative to the inflowing seawater on each day. This is considered to be the baseline matrix altered by the physical-biogeochemical processes in the lagoon. The solid, colour coded lines indicate data distribution when individual physical-biogeochemical reactions dominate the carbonate system.

In studies of deeper coastal environments where only pelagic communities dominate, temperature drives short-term changes in the carbonate system (Dai et al., 2009). This study suggests that, in agreement with Jiang et al. (2011), within shallow nearshore systems, alterations driven by autotrophic benthic organisms may contribute most to ecosystem change.

5.3 Tidal influence

Overlaying the eularian carbonate system analyses during sampling periods highlights the tidal influence on the biological signal (Figure 12). The ebbing tide sampled on JD 213 exhibits a maximum lagoon DIC concentration of around $2090 \mu\text{mol kg}^{-1}$ at the start of observations (09.30) likely due to the overnight predominance of CR. The DIC concentration systematically decreases from that point throughout the day to around $1950 \mu\text{mol kg}^{-1}$ with an approximate linear trend of $-20 \mu\text{mol kg}^{-1} \text{ hr}^{-1}$ driven by autotrophic activity linked with increasing solar irradiance, which had a mean value of $580 \pm 42 \text{ W m}^{-2}$ ($\pm 1 \text{ s.d.}$, $n = 18$) over the period.

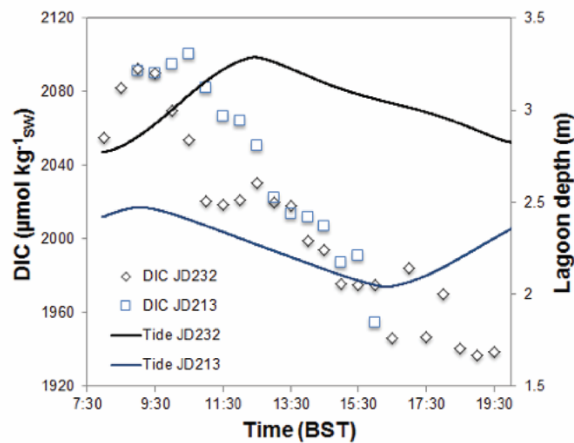


Figure 12. Lagoon tidal regime and observed inlet DIC concentration for both JD213 and JD232. A distinct pattern of diurnal biological production during the semi-diurnal tidal cycle fluctuation is present, indicating nutrient availability from tidal ebb and flood and daytime biology utilisation.

By comparison, during JD 232 when sampling started (08.00) on a flood tide, the DIC concentration within the lagoon initially increased from 2050 $\mu\text{mol kg}^{-1}$ to 2090 $\mu\text{mol kg}^{-1}$ due to a proportion of lagoon water that had earlier vacated the lagoon being forced back by the tide. Mixing of water carried back into the lagoon initially attenuates any biologically driven DIC concentration decrease. Net DIC loss becomes apparent after 09.30 when a sharp concentration drop was observed. The overall linear trend is approximately $-13 \mu\text{mol kg}^{-1} \text{ hr}^{-1}$ for a mean solar irradiance of $334 \pm 35 \text{ W m}^{-2}$ ($\pm 1 \text{ s.d.}$, $n = 25$). As the sampling occurred during daylight hours, primary production appears to be the driver of DIC concentration change over time at this site. In contrast, community respiration would be expected to dominate at night (Frankignoulle and Bouquegneau, 1990) and during winter periods (Delille, Borges and Delille, 2009).

5.4 Diel NEP rate

The contribution of atmospheric carbon via CO_2 transfer from atmosphere to the lagoon during the sampling period was estimated to be 4.3% of NEP. Conceivably, this is as a direct result of the photosynthetic uptake in the Inland Sea. Jiang et al. (2011) and Muduli et al. (2013) report similar findings, with CO_2 transfer from the atmosphere playing a significant role in the latter study. In this study we determined a positive NEP of $3.0 \pm 0.4 \text{ mmol C m}^{-2} \text{ hr}^{-1}$, which indicates a net carbon sink due to primary production during daytime. This is the average ecosystem metabolism during the photic semi-diurnal period of study (12.12 hr). Therefore, approximately 96% of the daytime carbon NEP budget in the lagoon was supported by DIC availability from advected nutrients while the remainder came from surface interface atmospheric CO_2

transfer. The estimated time-integrated metabolic rate for the 13.5 hr total daylight period is then equivalent to $40.5 \pm 5.4 \text{ mmol C m}^{-2}$.

We lack site-specific information on CR, however, Hopkinson and Smith (2005) report pelagic respiration rates in shallow inshore waters of between 58 and 114 $\text{mmol C m}^{-2} \text{ d}^{-1}$. Thus, assuming an overnight CR range of 2.42 – 4.75 $\text{mmol C m}^{-2} \text{ hr}^{-1}$ NEP estimates during our study period would yield values between 15.23 and -9.24 $\text{mmol C m}^{-2} \text{ d}^{-1}$. Whereas using a CR value of $279 \pm 184 \text{ mmol O}_2 \text{ m}^{-2} \text{ d}^{-1}$ ($n = 7$) measured in *Z. noltii* meadows in the Thau lagoon, France, and a photosynthetic quotient of 1 (Duarte et al., 2010), a time-integrated CR of $122 \pm 81 \text{ mmol C m}^{-2}$ can be calculated over the 10.5 hr respiration-dominated night-time period. This then suggests a diel NEP rate of approximately $-82 \pm 81 \text{ mmol C m}^{-2} \text{ d}^{-1}$ for our study site; the former range of estimates being more consistent with the median NEP value of 20.6 $\text{mmol C m}^{-2} \text{ d}^{-1}$ reported in seagrass ecosystem studies (Johnson et al., 2017).

Tokoro et al. (2014) presented global seagrass ecosystem NEP rates of $27 \pm 6 \text{ mmol C m}^{-2} \text{ d}^{-1}$ converted from oxygen-based units. NEP estimates and errors may vary dependent upon applied method and location. For example, Gazeau et al. (2005) found that measured NEP rates fluctuated between $7 \pm 1 \text{ mmol C m}^{-2} \text{ d}^{-1}$ and $41 \pm 3 \text{ mmol C m}^{-2} \text{ d}^{-1}$, with a mean of $22 \pm 12 \text{ mmol C m}^{-2} \text{ d}^{-1}$. Estimates of water residence times, which are difficult to quantify in open embayment's, contributed most to uncertainty. Ribas-Ribas et al. (2011) found NEP values between 10 and 60 $\text{mmol C m}^{-2} \text{ d}^{-1}$ neglecting the influence of water residence time. Other studies have assessed whether net autotrophic or heterotrophic behavior dominates in coastal systems based on longer studies of NEP, estimated from rates of GPP and CR, with GPP known to vary inter-annually by as much as 35% and NEP by 87% (Champenois and Borges, 2012).

The intertidal beds of the Inland Sea are colonized by the seagrass *Zostera noltii*, which contribute to primary production in the study area. Papadimitriou et al. (2006) estimated an increase in the above-ground seagrass biomass equivalent to 18 – 27 $\text{mmol C m}^{-2} \text{ d}^{-1}$ and in the below-ground biomass (roots and rhizomes) equivalent to 22 – 28 $\text{mmol C m}^{-2} \text{ d}^{-1}$ during growth periods in spring and summer. Duarte et al. (2005) reported on GPP, CR, and NEP for seagrass species and found that, in general, seagrass meadows with $\text{GPP} \geq 180 \text{ mmol C m}^{-2} \text{ d}^{-1}$ were net autotrophic. Specifically, for *Z. noltii*, ~66% of the meadows included in the Duarte et al. (2010) study had GPP values of this magnitude, attesting to the potential for carbon sequestration for this species of seagrass. Based on the limited daytime NEP data and assumed night-time CR of Duarte et al. (2010), the seagrass community in our study site may be net heterotrophic on an annual time scale but more detailed investigation is required to validate this indication. Thus, future modelling of lagoon systems would benefit from

diurnal and seasonal sampling of the CO₂ system to obtain annual estimates of net carbon gain or loss to the atmosphere and to the adjacent Irish Sea waters.

5.5 Residence time

The box model approach utilized here allows us to quantify the input and output of CO₂ in the system from both advective lateral fluxes and surface transfer regimes, which is crucial in shallow nearshore ecosystems. However, it requires the ability to accurately predict water flow through the channels, because large uncertainties are introduced into calculations over short time scales (Borges et al., 2008). By considering an integrated approach over a tidal period, the uncertainty is somewhat attenuated. The integrated mean used to derive mass balance calculations are based on polynomial fits of the plotted observational data, with 95% confidence intervals of the standard deviation of the slope used to constrain NEP calculations.

Based on simplified unidirectional, unforced and hydrostatically balanced channel flow calculations ($0.5 u^2 = -g d\eta/dx$) the contribution to error from uncertainty in harmonic boundary forcing in the MATLAB simulations causes a maximum elevation uncertainty of approximately 10 cm. This yields a maximum potential flow uncertainty of around 0.14 m s⁻¹ in a channel of 100 m length (this error reduces for longer channels). However, validation data resolution was of the same order of magnitude, therefore this was ignored for NEP error estimate. The largest contribution to uncertainty for this study came from the estimated lagoon phase error of 0.11 ± 0.09 hr ($n = 9$). Assuming an average flow through the channel over the error phase period of 0.5 m s⁻¹ (i.e. around slack water), a maximum difference in ΔF_{MIX} of approximately 0.15 mmol C m⁻² is possible. Therefore, greatest uncertainty is derived from the change in water residence time with phase shift. This results in an increase in the cumulative error estimation from ± 0.03 mmol C m⁻² hr⁻¹ to ± 0.4 mmol C m⁻² hr⁻¹ for a calculated difference in mean residence time of approximately 6 hours.

Based on a fixed tidal period and using the methods of this study, water residence time will increase if mean lagoon capacity increases or if the change in channel volumetric flow decreases (effectively a decrease in tidal range). An increase in residence time subsequently reduces NEP as the nutrients within the system take longer to be replenished and may result in a loss of seagrass habitat (Orfila et al., 2005). Delhez et al. (2014) report that the total time spent within the control domain may be significantly underestimated in oscillating flow regimes using the approach presented. It should be noted that calculation of residence time based on eq (6) utilizes the simple assumption that all of the water is exchanged through the channel, when in reality some of the water exiting or entering the lagoon returns immediately. A better approach may be to consider the fractional return of some of the water to avoid

overestimation of NEP (Sheldon and Alber, 2006; Rynne et al., 2016). Future work should focus on constraining the parameters critical to estimating the time taken for water to be replenished within the lagoon. Increased understanding of the lagoon bathymetry, channel dimensions and substrate type would all conceivably contribute to a reduction in modelled phase error.

6. Conclusion

Restricted lagoons such as the Inland Sea offer the ability to examine the variation in NEP from DIC utilization and water residence period due to the nature of their water exchange regimes. Increased high-resolution temporal monitoring using autonomous techniques may be beneficial, as would constraining spatial distribution of carbonate system concentrations. It has been shown that the overall net carbon productivity of the Inland Sea ecosystem can be assessed over a complete tidal period by conducting measurements of carbonate system parameters from water advected through the channels, in combination with post observation, bulk parameterization analysis. Development of methods should include autonomous measurements, improved geophysical evaluation, enhanced validation and numerical hydrodynamic modelling of boundary exchange, in order to further constrain estimates. Extrapolation of calculated values for increased spatial and temporal assessment should also be a future objective.

The overall net autotrophic balance of the seagrass containing system studied suggests a potential sink for inorganic carbon during summer periods. An estimated NEP of $40.5 \pm 5.4 \text{ mmol C m}^{-2}$ during the 13.5 hr daytime study period is equivalent to a diel range of between 15.23 and $-9.24 \text{ mmol C m}^{-2} \text{ d}^{-1}$ based on assumptions using reported shallow water pelagic respiration rates. However, it is crucial to include measurements of actual overnight respiration rate during studies, as a potential source of inorganic carbon is calculated ($-82 \pm 81 \text{ mmol C m}^{-2} \text{ d}^{-1}$) when literature values for *Zostera noltii* meadows based on O_2 utilization is assumed. Furthermore, the former approach suggests that approximately 4% of DIC is provided by CO_2 transfer from atmosphere to ocean during the study period. Similar methodology may provide an opportunity to assess the atmospheric carbon sequestration potential of planned nearshore lagoon constructions. From the MRE perspective, there exists the potential of enhancing the financial feasibility of tidal range lagoon energy schemes through consideration of carbon offsetting. In particular when such structures are designed to accommodate colonies of productive autotrophic flora.

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 928
 929 **Tables and Figures⁺**
 930 ⁺Colour to be used for Figures except 2, 3 and 5.